Origin of carbon in aromatic and olefin products derived from HZSM-5 catalyzed co-pyrolysis of cellulose and plastics via isotopic labeling

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A B S T R A C T

Catalytic pyrolysis over HZSM-5 is an effective method for the conversion of biomass to aromatic hydrocarbons, albeit with low yield and short catalyst lifetimes. Addition of co-reactants rich in carbon and hydrogen can enhance yield and possibly increase catalyst lifetimes by reducing coke formation. Particularly, the catalytic co-pyrolysis of plastic and biomass has been shown to enhance conversion to aromatic hydrocarbons, and also offers a method for productive disposal of waste agricultural plastics. In an effort to determine the origin of the carbon (plastic or biomass) in the products from this catalytic co-pyrolysis, mixtures of uniformly labeled ^{13}C cellulose and non-labeled plastic including polyethylene terephthalate, polypropylene, high density polyethylene, low density polyethylene and polystyrene were subjected to catalytic fast pyrolysis (CFP) at 650 °C in the presence of HZSM-5. A micro pyrolyzer coupled with GC/MS (py-GC/MS) advised product distributions and mass spectral data was used to determine the distribution of biogenic carbon and plastic derived carbon in the products. The results demonstrate that aromatic hydrocarbon products formed from the CFP of mixtures of cellulose and plastic are composed mostly of molecules containing carbon of mixed origin. Data on the distribution of $^{13}C_x\,^{12}C_y$ from the products followed in this study show that polyolefin mixtures with cellulose favor the formation of alkyl benzenes that incorporate carbon from both sources. Utilization of aromatic polymers (polystyrene or polyethylene terephthalate) is more selective for formation of naphthalenes with carbon derived from both products. The distribution of various $^{13}C_x\,^{12}C_y$ products is used to suggest active mechanisms that result in the formation of the observed products.

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1. Introduction

Pyrolysis, which is the thermal processing of material in the absence of oxygen can reduce waste by weight and volume and produce gases, solids and liquids which can be used as fuel or feedstock for chemical conversion [1]. The liquids produced from the pyrolysis of lignocellulosic biomass, called pyrolysis oil or bio-oil, are potential intermediates for production of drop-in renewable advanced hydrocarbon biofuels. However, incompatibility with hydrocarbons and instability resulting from a high concentration of reactive oxygenated components has limited the utility of pyrolysis oil to date. Much research has been done on catalytic fast pyrolysis (CFP), in an effort to produce deoxygenated pyrolysis liquids with more favorable properties. HZSM-5 which can produce aromatic hydrocarbons from biomass has been the most studied catalyst for this process [2–9] but is plagued by short catalysts lifetimes and

low carbon efficiencies. These problems are associated with the low H/C ratio of biomass; dehydrogenation and dehydration reactions catalyzed by HZSM-5 further reduce the hydrogen content, leading to coke formation. It is possible that incorporation of carbon and hydrogen rich co-reactants into the CFP process with biomass could help mitigate these problems; such a material could be waste agricultural plastics.

Farmers rely on plastics to increase crop yields, reduce the use of herbicides and pesticides as well as to conserve water [10]. Approximately two million tons of agricultural plastics are used annually worldwide [11] and an estimated 521 million pounds of agricultural plastics are used in the U.S. per year alone [3]. Utilization of waste plastics in this manner could have the added benefit of alleviating a major waste disposal problem for farmers in a meaningful way. Current methods for disposing of agricultural plastic waste include on farm incineration, burial or disposal in landfills [12]. Unfortunately, efforts toward the recycling of agricultural plastic waste [13–15] encounter many barriers which lead to increased costs for processing recycled plastics [16]. While incineration can produce usable energy it also releases toxins [17–19]. However,

pyrolysis produces fewer toxins due to the absence of oxygen and furthermore pyrolysis processes can handle mixed plastic waste with as much as 20% dirt or soil containments [20].

Pyrolysis of plastics has been conducted in the presence of catalysts to increase the production of desirable hydrocarbons for fuel [21–24] and catalytic co-pyrolysis of plastics and biomass or its constituents have been shown to increase aromatic product yields [25–28]. Plastic, catalyst and temperature were varied in experiments of the catalytic co-pyrolysis of pine sawdust and plastics [28]. The catalyst with the best performance was LOSA-1, which is made up of mostly ZSM-5, and doubled the petrochemical yields in these experiments [28]. Initial studies on the catalytic co-pyrolysis of low density polyethylene (LDPE) and cellulose in the presence of ZSM-5 gave increased aromatic carbon yields and reduced coke/char formation [25]. Cellulose was further investigated along with lignin and pine wood in combination with various plastics in catalytic co-pyrolysis and a synergy was found between cellulose and LDPE for petrochemical production and a reduction in coke formation [27]. An increase in aromatic products was found when comparing the co-fed CFP product yields to the additive yields of the CFP of the cellulose or biomass and plastics alone. In particular, combinations with polyethylene (PE) exhibited increases in alkylbenzenes [26]. It has been suggested that the formation of a hydrocarbon pool increases the conversion of oxygenates to aromatics [25,26]. The mechanisms thought to be involved in the catalytic conversion of cellulose through the formation of the hydrocarbon pool have been illustrated previously in the literature [29]. However, the results from these studies [25–28] do not indicate the amount of cellulose and plastic derived carbon that is contained in the products. An effective method for gaining insight on the mixing of reactants to form the products of pyrolysis involves the use of isotopically labeled reactants [30–32]. In this study the catalytic co-pyrolysis of ^{13}C labeled cellulose with several different plastics including polyethylene terephthalate (PET), polypropylene (PP), high density polyethylene (HDPE), LDPE and polystyrene (PS) were compared. Using mass spectral data from py-GC/MS experiments, the ratios of plastic and cellulose derived carbon that produced the condensable aromatic hydrocarbons such as benzene, toluene, ethylbenzene, *p*-xylene, *o*-xylene, naphthalene and 2-methylnaphthalene via CFP were determined. Also, the formation of non-condensable pyrolysis products including carbon monoxide, carbon dioxide, methane, ethylene, ethane, propylene, propane and butane were studied. Experiments were conducted using an identical non-labeled cellulose to serve as a calibration of the mass spectra data. The information was used to suggest active reaction mechanisms for each combination that lead to the yield and selectivity enhancements observed.

2. Experimental

2.1. Materials

Polyethylene terephthalate (PET), granular was purchased from Sigma-Aldrich and was milled using a Thomas Wiley ® Mini Mill with a delivery unit size of 0.85 mm, U.S. Std. no. 20. Polypropylene (PP), amorphous (avg. *Mw* ∼14,000; avg. *Mn* ∼ 3700 GPC vs. polyethylene stds.) was purchased from Sigma-Aldrich and was pliable at room temperature. A pellet was pressed flat using a spatula and then strips of PP were cut using scissors. The PP strips were then cut into smaller pieces (∼1–2 mm) using scissors. High density polyethylene (HDPE) (melt index 2.2 g/10 min (190 °C/2.16 kg)), low density polyethylene (LDPE) (melt index 25 g/10 min (190 °C/2.16 kg)) and polystyrene (PS) (avg. *Mw* ∼ 192,000) were purchased from Sigma-Aldrich and were milled using a Wiley Mill No. 1 (Arthur H. Thomas Co.,

Philadelphia, PA, U.S.A.) with a mesh size of 0.5 mm. Uniformly labeled ^{13}C cellulose high DP (97 atom% ^{13}C) from *Zea mays* (^{13}C cellulose) as well as the identical non-labeled cellulose high DP (1.2 atom% ^{13}C) from *Z. mays* (NL cellulose) were purchased from Iso*Life*. Zeolite NH$_4$ZSM5 powder (CBV 2314) was purchased from Zeolyst International and was converted to HZSM-5 by heating the powder to 650 °C overnight. The HZSM-5 was heated to over 100 °C for at least 2 h to remove water prior to using in experiments. The Si/Al ratio of the HZSM-5 was 23.

2.2. Pyrolysis

Pyrolysis experiments were conducted using a Frontier Lab Double-Shot micro pyrolyzer PY-2020iD equipped with the Frontier Lab Auto-Shot Sampler AS-1020E coupled to a gas chromatograph, Shimadzu GC-2010 [33–35]. Pyrolysis products were detected using a Shimadzu GCMS-QP2010S mass spectrometer (MS). For these experiments, the micro pyrolyzer was set to an interface temperature of 325 °C and a furnace temperature of 650 °C. Mixtures of ^{13}C cellulose or NL cellulose (0.250 mg) with plastic (1.3:1 cellulose (^{13}C):plastic (^{12}C)) and HZSM-5 (7.5 mg) were added to a stainless steel sample cup (Disposable eco-cup LF purchased from Frontier Laboratories). The sample is constructed by first placing the plastic in the sample cup followed by the biomass and then finally the catalyst on top. The sample is not initially mixed and is placed in the Auto-Shot Sampler. The sample is gravity fed into the inert atmosphere of the pre-heated pyrolysis furnace (650 °C), where the sample is subjected to pyrolysis conditions for 18 s. The helium carrier gas is also used to purge air in the sample prior to pyrolysis and to convey the pyrolysis gas through the pyrolysis reactor, a quartz tube, then to the GC–MS. GC analyses for the condensable gas products were performed on a RTX-1701 60 m × 0.25 mm, 0.25 m film thickness GC fused silica capillary column. The oven was programmed to hold at 45 °C for 4 min and ramped at 3 °C/min to 280 °C, after which it was held at this temperature for 20 min. The injector temperature was kept at 250 °C with the injector split ratio set to 90:1 and the helium flow rate was maintained at 1 mL/min. MS detection was carried out under electron impact (EI) ionization conditions in full scan from *m/z* 35–500 with a threshold at 20. GC analysis was performed using a fused silica capillary column, CP-PoraBOND Q, 25 m × 0.25 mm (Varian, Palo Alto, CA) with the following program: 3 min at 35 °C then ramped at 5 °C/min up to 150 °C followed by 10 °C/min up to 250 °C and held for 45 min for a total run time of 81 min. MS detection was carried out under electron impact (EI) ionization conditions in full scan from *m/z* 14–350 with a threshold at 1000.

2.3. Quantification

CFP experiments CFP of ^{13}C cellulose with plastics were performed in triplicate and the mass table data for a particular product was utilized to quantify the amount of ^{13}C from ^{13}C cellulose and ^{12}C from plastic in each of the products analyzed. For the determination of yields, experiments with an identical NL cellulose were performed in triplicate and the weight percent (wt%) yields were quantified with calibration curves produced using internal standards of the condensable gas products toluene, ethylbenzene, *p*-xylene, *o*-xylene, naphthalene and 2-methylnaphthalene. The gas yields were quantified with calibration curves produced using a standard gas mixture comprising CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, and C_4H_{10} in helium (custom-mixed by Scott Specialty Gases, Plumsteadville, PA). The carbon yields, determined from wt% yields, are presented as averages and were calculated as previously described [26]. Determinations of distribution of ^{13}C and ^{12}C carbon in each product were done using mass
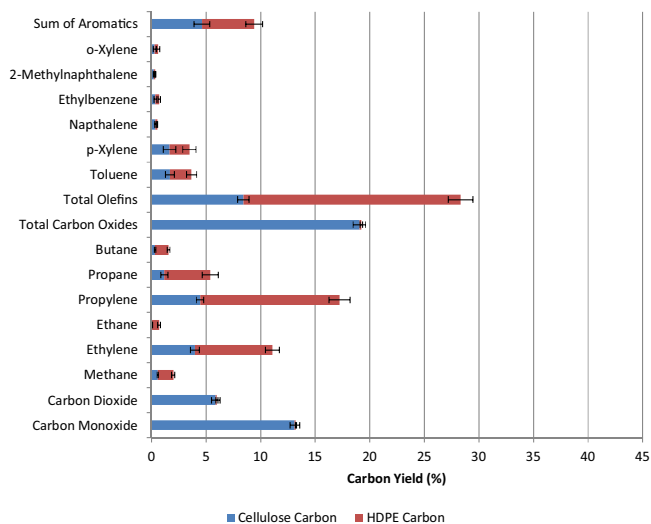
Fig. 1. The distribution of carbon from cellulose and carbon from HDPE in the condensable and non-condensable gas products from the CFP of both feedstocks in the presence of HZSM-5.

Fig. 2. The distribution of carbon from cellulose and carbon from LDPE in the condensable and non-condensable gas products from the CFP of both feedstocks in the presence of HZSM-5.

spectral data that was analyzed as described in the supplementary data.

3. Results and discussion

3.1. Carbon yields

The CFP of biomass and plastic over HZSM-5 leads to the production of aromatic hydrocabons, with a yield enhancement or selectivity change over the sum of their individual CFP products. This effect is thought to be due to enhanced conversion of biomass carbon to aromatics at the expense of coke formation due to the higher concentration of hydrocarbon reactants in hydrocarbon pool pathway to aromatics [25–28]. Coke formation is an important factor when considering catalytic pyrolysis as it deactivates the catalyst and shortens its lifetime. The reduction of coke during the catalytic co-pyrolysis of biomass and plastics should aid in extending catalyst life-time and improve the yields of the desired products. This isotopic labeling study allowed for further probing of the fate of the biogenic carbon. When mixtures of ^{13}C cellulose and plastic were subjected to CFP they produced aromatic hydrocarbons which contained molecules of mixed origins. Overall, for the mixtures of cellulose and plastic, the amount of biogenic carbon in the six aromatic hydrocarbons studied here was 49% for HDPE, 52% LDPE, 59% for PP, 55% for PS and 65% for PET as shown in Figs. 1–5. When considering that approximately 56% of the carbon in each pre-pyrolyzed mixture was ^{13}C from cellulose, this translates to PE and PS mixtures producing the highest yield of biogenic carbon in the aromatic products (8.2% for HDPE, 8.8% for LDPE and 8.6% for PS) and PET mixtures being the least effective at aiding the conversion of the biogenic carbon into aromatic products, with a biogenic carbon yield of 3.8%. While PP had a relatively high yield of biogenic carbon in the resulting aromatic products (5.1%), this did not surpass those produced by mixtures with PE or PS. The use of PE or PP as a co-reactant is thought to aid the conversion of biomass during CFP by adding olefins to the hydrocarbon pool which can react with the oxygenated biomass primary pyrolysis products to avoid coke formation [25,26,29]. The pyrolysis of non-polyolefin polymers (PS, PET) produces a lower concentration of olefins to contribute to that pool, lessening their potential to interact in this manner [32,36,37].
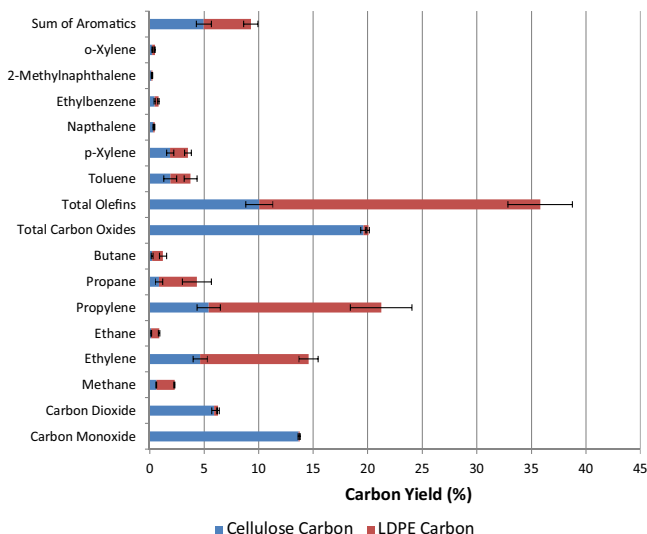
Using the mass spectral data, it is also possible to determine the origins of the carbon that makes up the individual products of the CFP of the blends. For example, when PS was co-pyrolyzed with cellulose, 80% of the carbon in the *p*-xylene formed was biogenic while about 60% of the toluene carbons were biogenic (Fig. 4). Other work on the pyrolysis of PS showed that pyrolysis PS at 600 °C produced between 83 and 87 wt% styrene monomer via simple depolyemrization for polymers with a molecular weight of 1.1×10^5 and 3.8×10^5, respectively [36]. Styrene is not a likely intermediate for the formation of other alkyl benzenes over HZSM-5 and therefore explains the large percentage of the cellulose derived carbons in the toluene and xylenes. It also explains why the PS blends produced the highest selectivity for naphthalenes over alkyl benzenes. Also consistent with this observation is that CFP of the PS blends produces significantly fewer olefins (~10% total C yield) than does the CFP of the PE or PP blends (25–35% C yield). However, the selectivity for the production of toluene for PS blends is significantly greater than for PET and PP. This may indicate that PS pyrolysis products
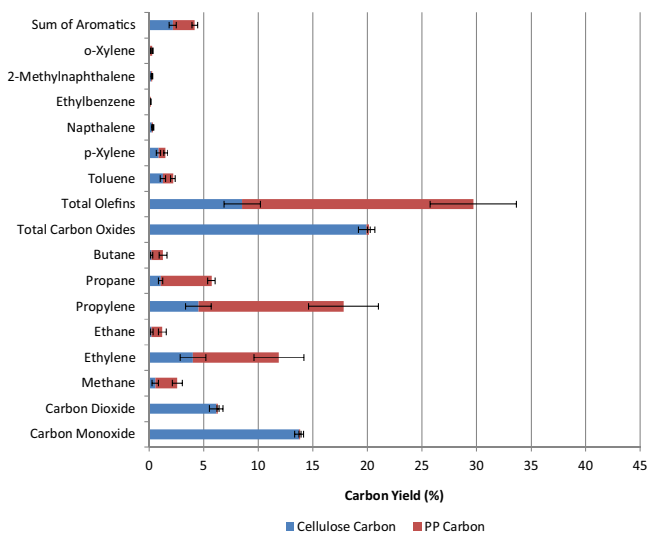

Fig. 3. The distribution of carbon from cellulose and carbon from PP in the condensable and non-condensable gas products from the CFP of both feedstocks in the presence of HZSM-5.
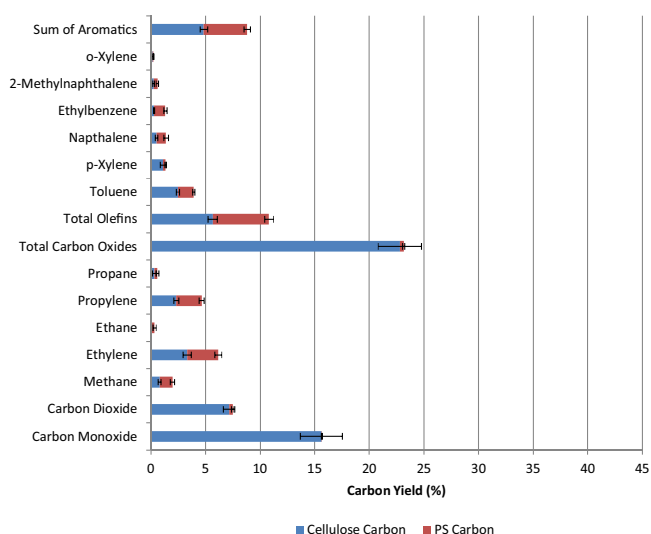
Fig. 4. The distribution of carbon from cellulose and carbon from PS in the condensable and non-condensable gas products from the CFP of both feedstocks in the presence of HZSM-5.

may influence the pathway of the cellulose CFP toward producing toluene, though contributing less carbon to it. PS also produces the most ethylbenzene among the plastic–cellulose mixtures with the majority consisting of all ^{12}C (PS derived) ethylbenzene (78%). This may indicate that formation of ethylbenzene is derived mostly from the reduction of styrene produced from pyrolytic depolymerization of PS. As expected nearly all of the carbon oxide gases produced from the PS/cellulose blends are derived from cellulose and with more than 20% C yield of the carbon oxide gases, blends with PS produces the most versus all the other blends. This indicates that PS pyrolysis products do not act as direct reducing agents (oxygen acceptors) for deoxygenation of cellulose pyrolysis vapors nor does the presence of PS pyrolysis products effectively divert cellulose pyrolysis products from cracking reactions that produce carbon oxides.

PET is similar in structure to PS, with both containing aromatic rings, but the major difference being that PET also contains oxygen. Previous work has shown that the majority of products from the pyrolysis of PET at 600 °C consisted of carbon dioxide/acetaldehyde
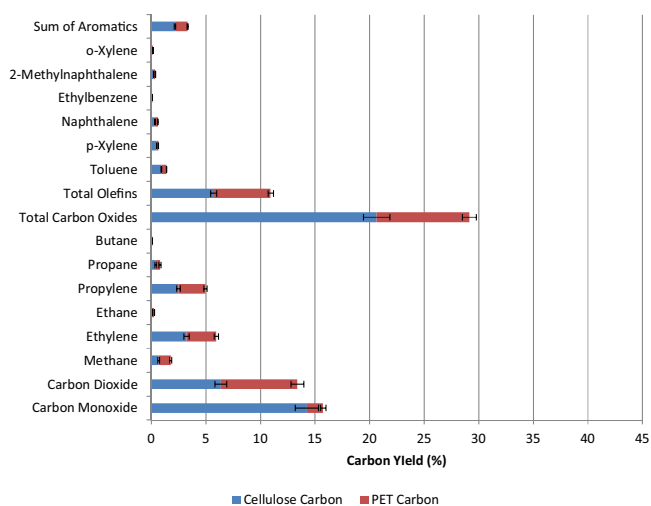

Fig. 5. The distribution of carbon from cellulose and carbon from PET in the condensable and non-condensable gas products from the CFP of both feedstocks in the presence of HZSM-5.

(20.73 wt%), 4-(vinyloxycarbonyl) benzoic acid (27.08 wt%), and benzoic acid (10.10 wt%) [37]. The results of which are verified with our non-condensable gas data in Fig. 5, showing that PET contributes the majority of the carbon in carbon dioxide formed from its CFP with cellulose. The yield of biogenic CO_2 in PET–cellulose mixtures is about the same as those that contain PS suggesting the presence of these plastics does not influence the yield of CO_2 from cellulose. Like PS the conversion of PET to olefins by pyrolysis is low, and therefore has less influence on the formation of alkyl benzenes through the aforementioned hydrocarbon pool mechanisms [25,26,29]. The yield of aromatic products from PET is lower than that of PS but the distribution of cellulose or PET carbon into the aromatic products is similar to that of PS, with the exception of ethylbenzene, which is composed of more biogenic carbon than PET carbon.

For the polyolefin (PE and PP) blends, the results are drastically different than for those with the aromatic polymers. The permanent gas products of PP and the PEs are very similar in the overall amounts and distributions (Figs. 1–3) with olefins such as ethylene and propylene being produced in large amounts and made up of mostly carbon from the corresponding plastic. Production of these olefins leads to production of the largest amounts of toluene and p-xylene among all the plastics that can participate in the formation of aromatics via HZSM-5 catalysis [25–27,29]. The carbon monoxide and carbon dioxide yields are composed of mostly carbon from cellulose, with the total carbon yield of oxide gases being less than 20%, showing a slight decrease compared to PS and PET. This can be attributed to the combination of the small oxygenated species from the pyrolysis of cellulose combined with the olefins produced from the pyrolysis of these plastics [38,39] in a Diels–Alder type of reaction [40] to form aromatic products, subjecting fewer of the oxygenates to conversion to carbon oxides via cracking over HZSM-5 [25–27].

The PEs are far more efficient in aiding the conversion of cellulose and plastic to aromatic compounds producing approximately twice as much (9.42% for HDPE, 9.27% for LDPE) compared to PP (4.92%). PP, also known to produce mostly olefins during pyrolysis [39], produces similar amounts of olefins compared to the PEs with approximately 70% consisting of carbon from plastic but it has been determined that the pyrolysis of PP can produce up to 42 wt% 2,4-dimethyl-1-heptene [39], a relatively large (C9) molecule for conversion within the pores of HZSM-5. This may help explain the reduced conversion of PP carbon to aromatic products compared to the PEs. Overall, the mixtures containing polyolefins are more selective for the production of alkyl benzenes while the PS and PET are more selective for the production of naphthalenes. PS produces three times more naphthalene (1.39%) and twice as much 2-methylnapthalene (0.61%) as the other plastics with ∼60% of the carbon from these two products being derived from PS versus ∼60–70% biogenic carbon composition for the formation of these products in PP, PE and PET. Carbon yields for aromatic products from the catalytic fast pyrolysis of cellulose, PP, HDPE, LDPE, PET and PS are given in Table S5 in the supplementary data.

3.2. $^{13}C_x\,^{12}C_y$ product distributions and possible mechanisms

More detailed information can be obtained by examining the various distributions of $^{13}C_x\,^{12}C_y$ products from the CFP of ^{13}C labeled cellulose and plastic. Figs. 6 and 7 show that the formation of ethylene and propylene favors all ^{12}C olefins for PE and PP. This is due to the thermal degradation products of PE and PP consisting mostly of olefins [38,39]. The catalytic decomposition reactions of polyethylene or polypropylene in the presence of silica–alumina based catalyst have been discussed previously and can produce radicals, C_2–C_{11} alkanes and olefins, cycloalkanes, cycloalkenes, and aromatic hydrocarbons [41]. Specifically, the pyrolysis of
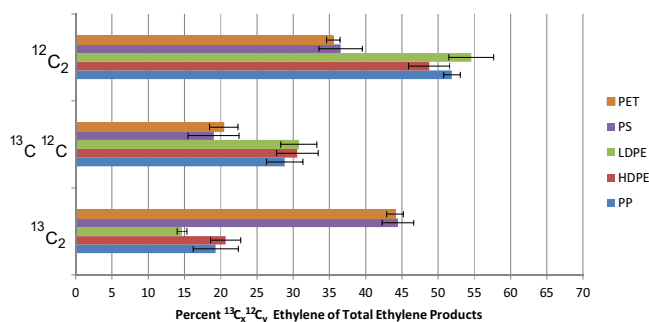
Fig. 6. Percent distribution of $^{13}C_x\,^{12}C_y$ ethylenes in the CFP of plastic (PET, PS, LDPE, HDPE, PP) and ^{13}C cellulose.
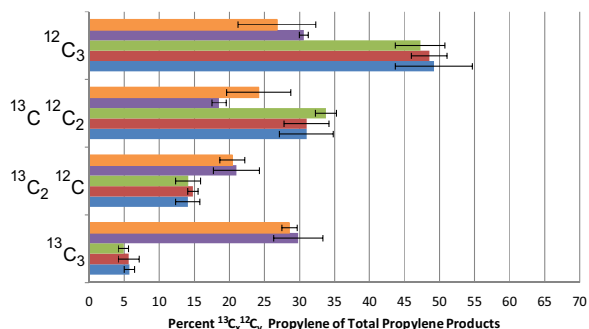

Fig. 7. Percent distribution of $^{13}C_x\,^{12}C_y$ propylenes in the CFP of plastic (PET, PS, LDPE, HDPE, PP) and ^{13}C cellulose.

polyethylene over HZSM-5 produces ethylene and propylene and these become present in greater amounts at higher temperatures [42]. Similar catalytic reactions of butene in the presence of ZSM-5 have been discussed in detail previously and can produce ethylene and propylene and can also be a direct source of aromatic hydrocarbons [43]. All ^{13}C ethylene and propylene can be produced from the conversion of cellulose pyrolysis products including furans over HZSM-5 [29] which show an increased selectivity for olefin production in the presence of HZSM-5 [44]. The presence of PS and PET enhances the production of all biogenic ethylene and propylene when these plastics are co-pyrolyzed with cellulose in the presence of HZSM-5.

Mixed benzene products, Fig. 8, are minimal for PET and PS with more than 50% of benzene produced from the co-pyrolysis of
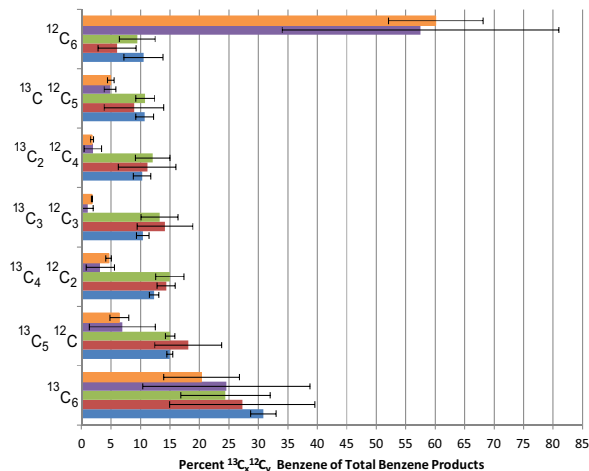

Fig. 8. Percent distribution of $^{13}C_x\,^{12}C_y$ benzenes in the CFP of plastic (PET, PS, LDPE, HDPE, PP) and ^{13}C cellulose.

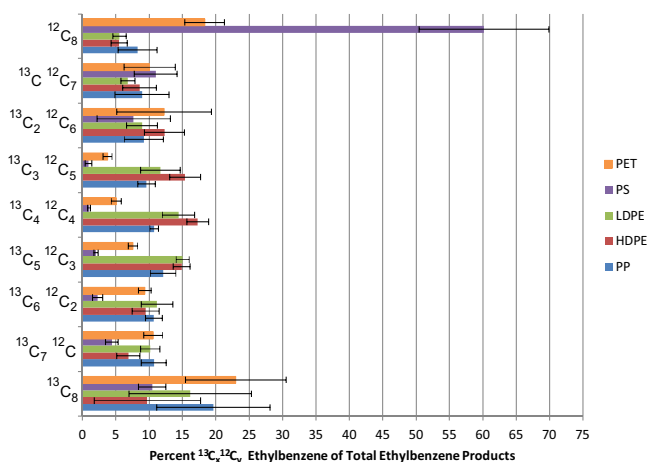**Fig. 9.** Percent distribution of $^{13}C_x\,^{12}C_y$ ethylbenzenes in the CFP of plastic (PET, PS, LDPE, HDPE, PP) and ^{13}C cellulose.

PET and PS with cellulose being all ^{12}C benzene due to the majority of the plastics' thermal degradation products being made up of larger aromatic hydrocarbons [32,36]. For the PS case, while small amounts of ethylene and propylene are produced from its catalytic degradation, styrene oligomerization, cracking, and hydrogen-transfer reactions in the presence of acidic catalyst are responsible for the formation of the major products benzene, toluene and ethylbenzene [45]. This is reinforced by the results in Fig. 9 that show that more than 60% of all the ethylbenzene produced when ^{13}C cellulose and PS undergo CFP is all ^{12}C ethylbenzene. This ethylbenzene is believed to be directly involved in the formation of naphthalene and 2-methylnaphthalene with a significantly greater amount of $^{13}C_2\,^{12}C_8$ naphthalene and $^{13}C_3\,^{12}C_8$ 2-methylnaphthalene being produced when cellulose is co-pyrolyzed with PS in the presence of HZSM-5 (Figs. 10 and 11). Mixed benzenes are formed mostly when PE and PP are present, but it is not more favorable than the production of all ^{13}C benzene from the co-pyrolysis of these plastics with cellulose. For toluene, ethylbenzene, p-xylene and o-xylene mixed products are favored for PP and PE over the production of all ^{12}C or all ^{13}C products (Figs. 12, 9, 13 and Fig. S5, respectively).

The observation of ethylene and propylene of mixed origins is evidence that the reaction mechanisms are more complicated than those mentioned previously [25–27]. The formation of mixed ethylene is possible through the oligiomerization/aromatization of the
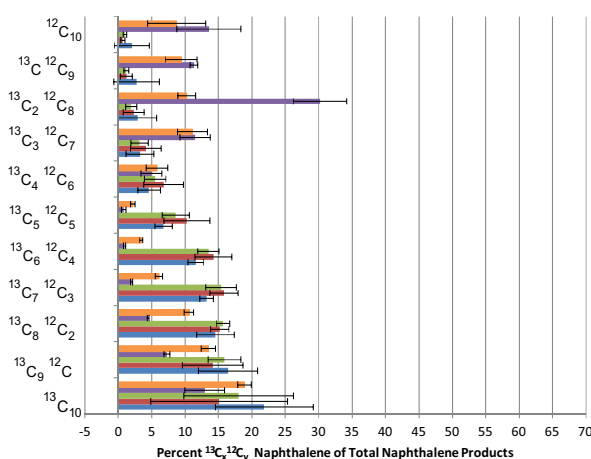

Fig. 10. Percent distribution of $^{13}C_x\,^{12}C_y$ naphthalenes in the CFP of plastic (PET, PS, LDPE, HDPE, PP) and ^{13}C cellulose.
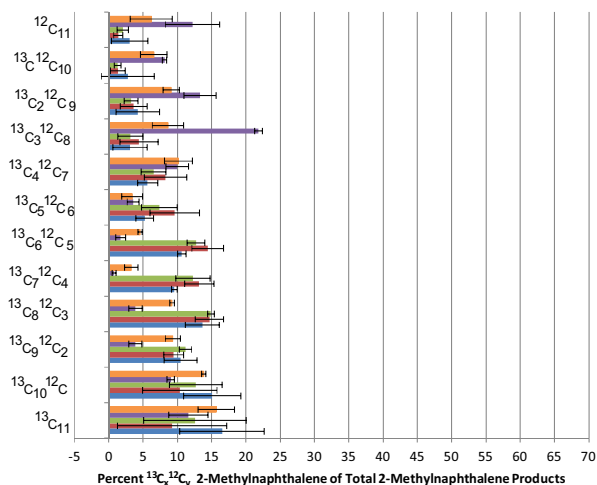
Fig. 11. Percent distribution of $^{13}C_x$ $^{12}C_y$ 2-methylnapthalenes in the CFP of plastic (PET, PS, LDPE, HDPE, PP) and ^{13}C cellulose.
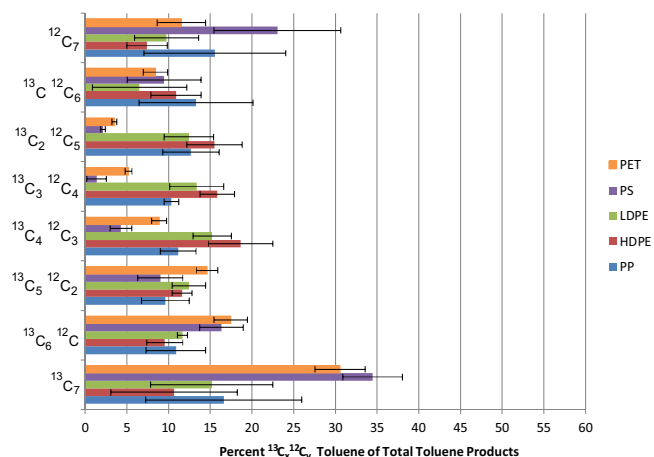

Fig. 12. Percent distribution of $^{13}C_x$ $^{12}C_y$ toluenes in the CFP of plastic (PET, PS, LDPE, HDPE, PP) and ^{13}C cellulose.

Fig. 13. Percent distribution of $^{13}C_x$ $^{12}C_y$ p-xylenes in the CFP of plastic (PET, PS, LDPE, HDPE, PP) and ^{13}C cellulose.

primary CFP products followed by re-cracking of these larger olefins and aromatics which then re-enter the hydrocarbon pool [46–48]. More recently a dual arene olefin cycle has been proposed [49] and ethylene and propylene have been proven to produce active hydrocarbon pool species [50]. It is therefore likely that ethylene and propylene from the various reactions that occur upon catalytic fast pyrolysis of ^{12}C polyolefins [41–43] can enter the same hydrocarbon pool as th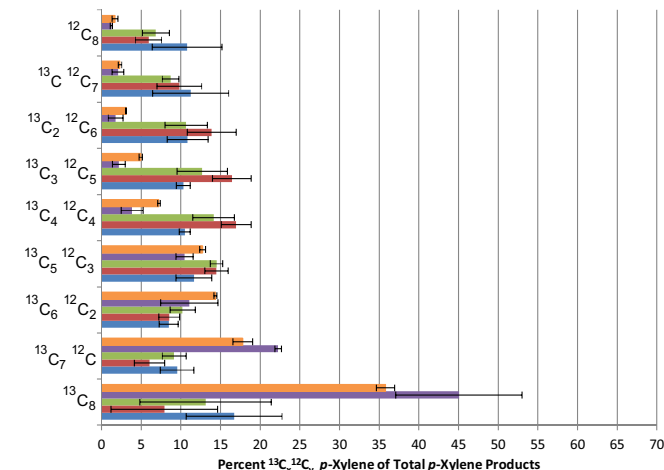e small molecules from the acid catalyzed reaction pyrolysis of ^{13}C cellulose [46] in the presence of HZSM-5 which would lead to the mixing of these two feedstocks found in the products of this study (Scheme 1). The mixed origin ethylene and other mixed origin olefins formed by similar pathways can reenter the cycle and are the source of the broad array of mixed aromatics formed as described in Figs. 8–11. In the CFP of LDPE and cellulose from our experiments there are significantly more small olefins produced than aromatic hydrocarbons with this ratio being significantly increased compared to experiments run under similar conditions but longer residence time [25]. This may further indicate that these olefins are intermediates to the formation of alkyl benzenes which are formed preferentially as the contact time with the catalyst increases via the hydrocarbon pool mechanism.

The combination of ethylene and propylene with furans produced from cellulose can also give benzene, toluene and xylenes via Diels–Alder cycloaddition reactions [40] (Scheme 2). PS and PET do not produce enough of the small olefins necessary for producing significant amounts of mixed aromatic hydrocarbons in this manner, Figs. 4 and 5, compared to PE and PP, Figs. 1–3. Production of mixed naphthalenes can also come from the Diels–Alder condensation and dehydration of benzene and furan as well as the successive alkylation of toluene with intermediate allene [40]. Scheme 3 shows how the formation of $^{13}C_2$ $^{12}C_8$ is possible from styrene, a major product from the pyrolysis of polystyrene [36], and the successive alkylation with allene [40]. The production of $^{13}C_3$ $^{12}C_7$ naphthalene from $^{12}C_7$ toluene from PS, which is shown to be a major product from the pyrolysis of PS and ^{13}C cellulose in Fig. 12, is also possible through this mechanism.
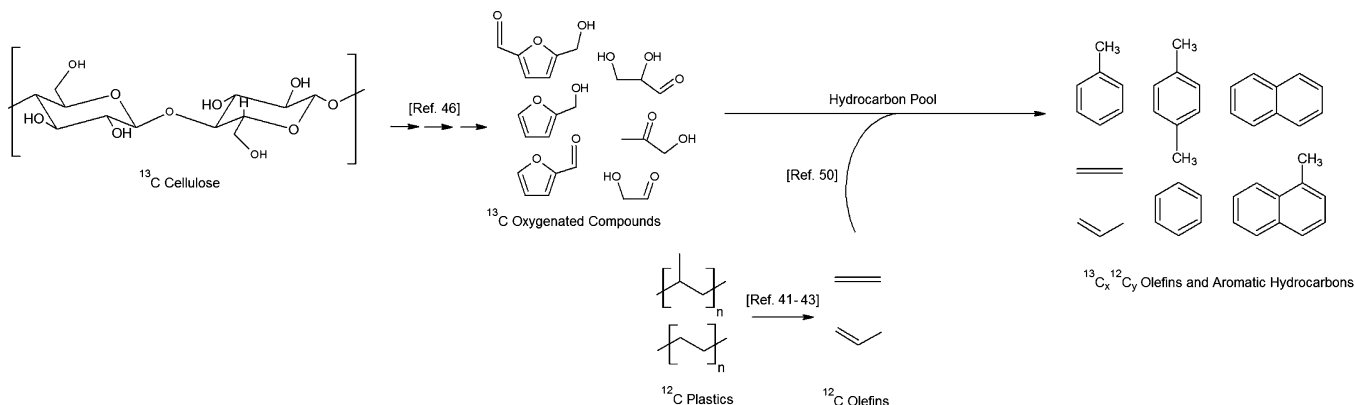
Scheme 1. Possible reaction pathway for the formation of mixed olefins and aromatic hydrocarbons from the catalytic fast pyrolysis of ^{13}C cellulose and ^{12}C plastics.
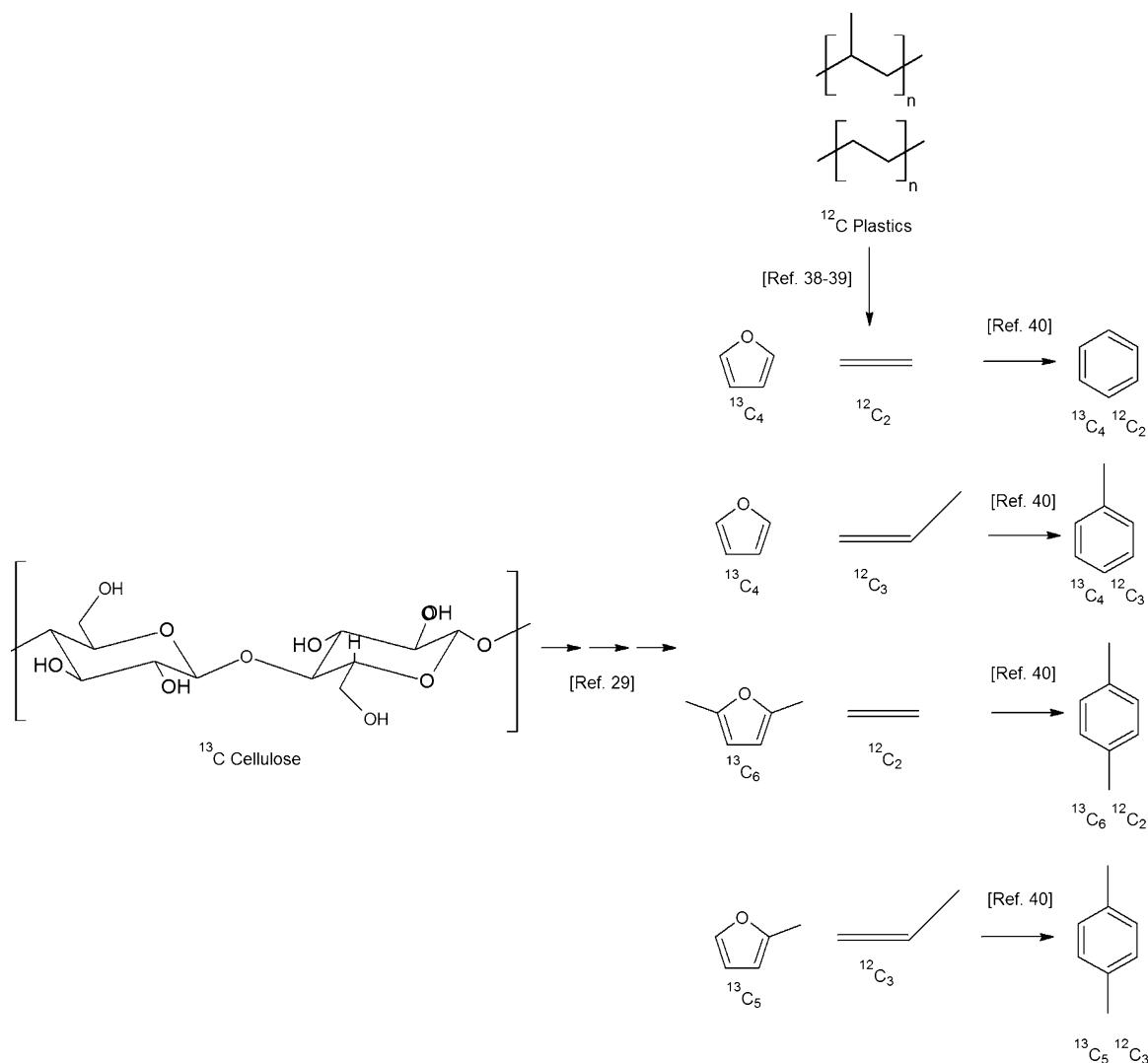
Scheme 2. Possible reaction scheme for the production of mixed benzene, toluene and *p*-xylene from CFP of ^{13}C cellulose and non-labeled PE and PP by Diels–Alder cycloaddition.
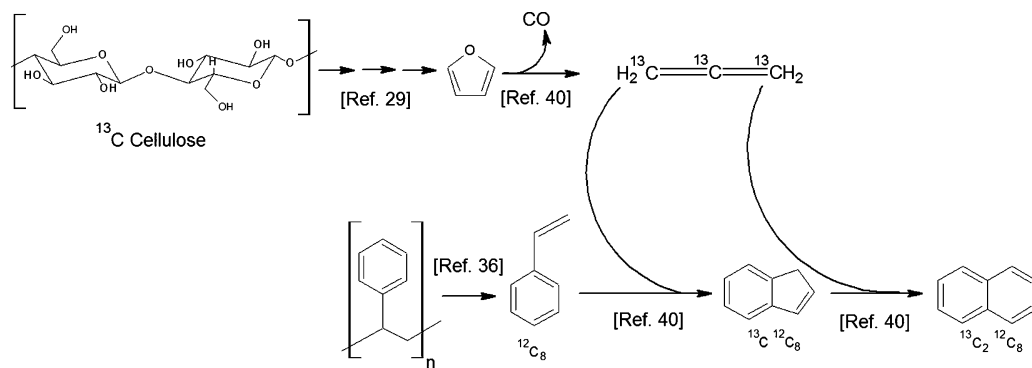
Scheme 3. Possible reaction scheme of the formation of $^{13}C_2$ $^{12}C_8$ naphthalene from the CFP of ^{13}C cellulose and non-labeled PS in the presence of HZSM-5.

4. Conclusion

Isotopic labeling experiments were used to determine the chemical influence of various plastic blends on the HZSM-5 mediated CFP of cellulose. These studies advised the distribution of biogenic and plastic derived carbon during pyrolysis of cellulose and plastic blends and provide insight into the active reaction mechanisms that account for observed product selectivity changes. For example, toluene, ethylbenzene and naphthalene are produced in greater amounts when PS is subjected to CFP with cellulose versus other plastics. Also *p*-xylene is produced in greater amounts for HDPE and LDPE blends than when other plastics are utilized. The ratio of biogenic to plastic derived carbon was higher in alkyl benzenes produced from mixtures containing PET or PS, while the

plastic derived carbon was found in higher concentration in the polyaromatic (naphthalenes) products. For the polyolefins, PEs particularly, the production of olefins to contribute to the hydrocarbon pool enhanced the conversion of biogenic carbon to alkylbenzens; toluene and *p*-xylene for the PEs were evenly made up of carbons from cellulose and the plastic with the remaining products being made up of slightly more cellulose derived carbon. Data on the distribution of all the possible $^{13}C_x\,^{12}C_y$ products show that overall mixing is favored for PE and PP with the smaller fragments from the pyrolysis of the plastics coming together with smaller fragments of cellulose to form toluene, ethylbenzene and *p*-xylene. These results suggest that if alkyl benzenes are a targeted deoxygenated biomass pyrolysis product, blending of polyolefins, especially PE, is recommended over blending of PS or PET. Blending becomes favorable for PS and PET with the larger aromatic hydrocarbons, naphthalene and 2-methylnaphthalene, where larger uniform ^{12}C fragments are necessary. The distribution of $^{13}C_x\,^{12}C_y$ in the various products gave insight into active reaction mechanisms revealing that many more reactions beyond the often sighted hydrocarbon pool mechanism are active. Ongoing research aims are to exploit the observations made here to advise the enhanced production of deoxygenated pyrolysis liquids and selective aromatic hydrocarbons from biomass and waste agricultural plastic via CFP processes.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at http://dx.doi.org/10.1016/j.apcatb.2014.07.006.

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